Phase Equilibria in the Al-Fe, Zn-Fe and Zn-Al-Fe Systems and Interfacial Reactions in Fe / Molten Zn Diffusion Couples

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論文内容要旨

Chapter 1 : Introduction

Steel sheet is one of the indispensable structure materials for the modern automobile industry due to its excellent mechanical properties which are available at a low cost. However, the low level of corrosion resistance is a problem in its service life. Therefore, investigation to improve the corrosion resistance of steel sheets is very important.

The coating method performed by dipping the steel sheet into molten Zn or Al alloys is one of post-treatments for steel sheets to improve the corrosion resistance in these days. The typical coating method is well-known as hot-dip galvanizing (GI) / galvannealing (GA) or hot-dip aluminzing (HDA). In hot-dipping method, intermetallic compound (IMC) layers are formed at the interface and mainly affect the corrosion resistance of coated steel. Therefore, formation behavior of IMC layers at the interface must be controlled for improving the life time. In order to understand the interface reactions in solid / liquid phases such as formation sequence and growth rate, the equilibrium phase diagram is important as fundamental data. Figure 1 shows

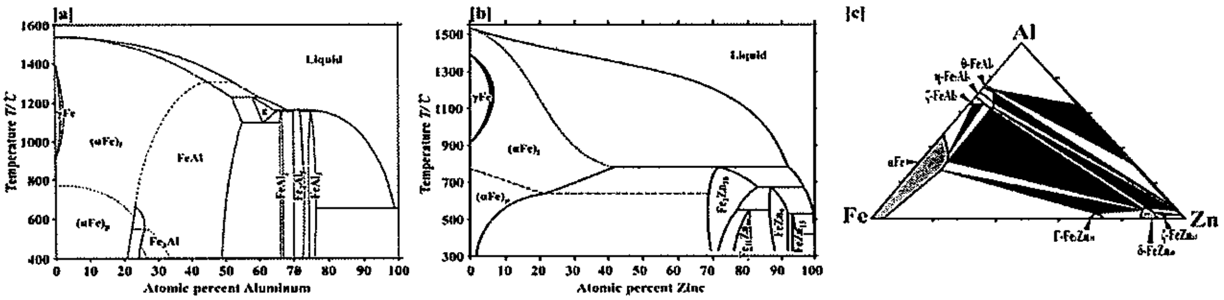

Figure 1 Previously assessed (a) Al-Fe [1], (b) Zn-Fe [2] and (c) Fe-Zn-Al [3] phase diagrams.

the phase diagrams of Al-Fe, Zn-Fe binary and Fe-Zn-Al ternary systems assessed by Kattner *et al.* [1], Burton *et al.* [2], Perrot *et al.* [3], respectively. Whereas widely received and used, these equilibrium phase diagrams have not been precisely determined by the alloying method due to the several problems. Owing to the strong tendency of oxidation in Al alloy, phase equilibria between IMCs in the Al-rich portion of Al-Fe binary system have not been studied precisely even though their importance related to the HDA process was widely recognized. On the other hand, in the phase diagrams of Zn-Fe based alloys, it is much difficult to determine the phase equilibria by alloying method, because of difficulty in fabrication of Fe-Zn alloys by conventional methods, since the boiling point of Zn (at 1.013×10^5 Pa), T_b=906℃ is extremely lower than the melting temperature of Fe, T_m=1536℃. Therefore, most of experimental data on phase equilibria including the solubility range of each IMC phase were determined by the diffusion couple (DC) method.

As describe above, although the hot-dip coating such as HDA and GI / GA process is recognized to be a promising method to improve the performance of steel sheet, fundamental research subjects, such as phase diagrams, interfacial reactions, mechanical properties of IMC layers, etc. have not been completed sufficiently even in the Al-Fe and Zn-Fe binary systems. Considering lack of the fundamental knowledge related to the hot-dip coating process, the following subjects were investigated in the present thesis.

- Experimental determination of phase diagrams of the Al-Fe and Zn-Fe binary systems, and Fe-Zn-Al ternary system by alloying method
- Investigation of Hardness of IMC phases in the Zn-Fe binary system
- Study on the interfacial reaction between solid Fe and molten Zn

Chapter 2 : Experimental determination of phase diagram of the Al-Fe binary system

In this chapter, the phase equilibria of the Al-rich portion in a composition range between 48 and 90.3at.%Al in the Al-Fe binary system were experimentally determined by conventional heat-treatment, the DC method and thermal analysis. Figure 2 shows the phase diagram experimentally determined for Al-rich portion of Al-Fe binary system. Solubility ranges of the ζ-$FeAl_2$, η-Fe_2Al_5 and θ-Fe_4Al_{13} phases in Al-Fe binary system are asymmetrical, and single-phase regions of the η and θ phases tended to incline toward the Fe-rich side with increasing temperature. In order to determine the equilibrium composition of the ε-Fe_5Al_8 phase, whose microstructure in two-phase alloys above the eutectoid temperature cannot be frozen even by rapid quenching, the DC method and thermal analysis was applied. The solubility of ε phase deviates to Fe-rich direction and the invariant reaction temperature of ε → α + ζ is also slightly higher than temperature previously reported by Kattner *et al.* [1]. On the other hand, the unidentified invariant reaction of θ phase was concluded by thermal analysis of DSC to be a peritectic reaction, Liquid + η → θ.

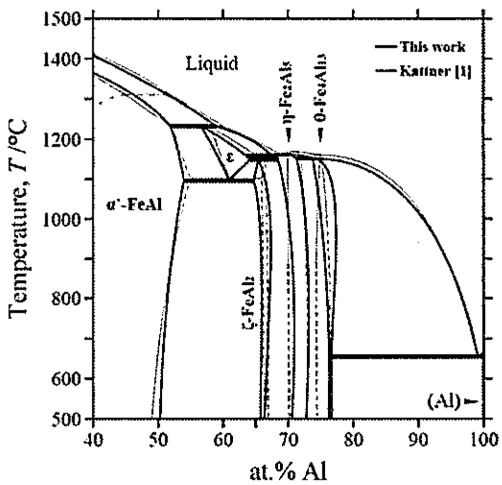

Figure 2 Experimentally determined phase diagram of Al-rich portion of the Al-Fe system

Chapter 3 : Determination of phase diagram of the Zn-Fe binary system

In this chapter, phase equilibria for αFe, Γ-Fe_3Zn_{10}, Γ_1-$Fe_{11}Zn_{40}$, δ_{1k}-$FeZn_7$, δ_{1p}-$FeZn_{10}$, ζ-$FeZn_{13}$ and liquid phases were determined by alloying method, employing a multi-step melting technique under vacuum and a 95%-argon-5% hydrogen atmosphere. Figure 3 shows the phase diagram of Zn-rich portion of Zn-Fe binary system determined. It is seen that the solubility ranges of IMCs determined in the Zn-rich portion entirely deviate to the Fe-rich portion in comparison with the Zn-Fe phase diagram assessed by Burton *et al.* [2]. In the present study, it was confirmed that the $\delta_{1p}+\delta_{1k}$ two-phase structure appears and that an eutectoid reaction, $\delta_{1p}\rightarrow\delta_{1k}+\zeta$, exists in the temperature range between 455℃ and 445℃.

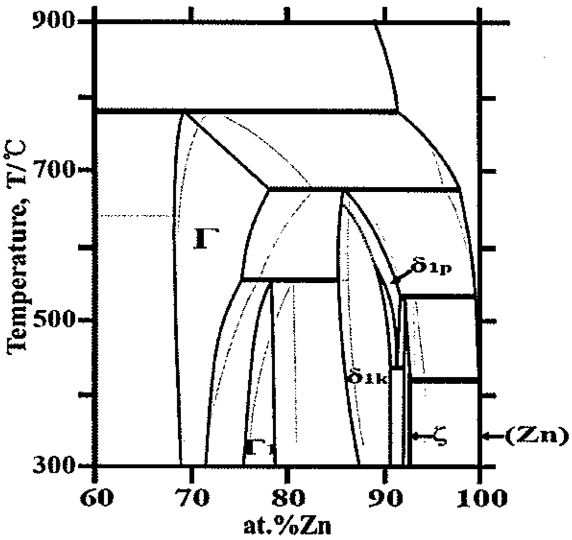

Figure 3 Experimentally determined Zn-Fe phase diagram in the present work.

Chapter 4 : Determination of phase diagram of the Fe-Zn-Al ternary system

In this chapter, phase equilibria at 450℃ in the Fe-Zn-Al ternary phase diagram were experimentally determined by the alloying method. The existing regions of three phase equilibria in Fe-Zn-Al ternary phase diagram are almost coincident with the phase diagram previously reported by Perrot *et al.* [3], but the solubility ranges are fairly different. Especially, the Γ_2 phase, which is formed in the liquid phase after a long reaction time in DC, was clearly observed in the alloy specimens as shown in figure 4, and it was confirmed that the single phase region is smaller than the previous result.

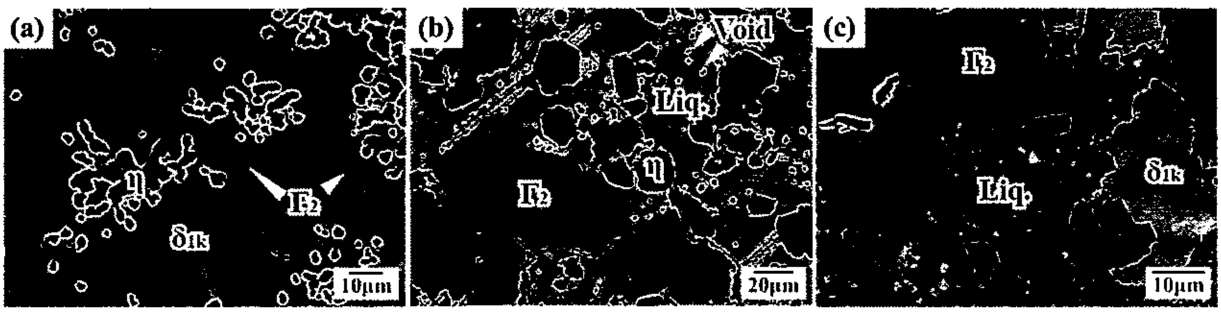

Figure 4 BSE images obtained from the ternary phase of Γ_2 in (a) 82.8at.%Zn-8.2at.%Fe-9at.%Al, (b) 93.1at.%Zn-3.9at.%Fe-3at.%Al and (c) 86.3at.%Zn-3.7at.%Fe-10at.%Al alloys annealed at 450℃.

Chapter 5 : Investigation of hardness of IMC phases in the Zn-Fe and Fe-Zn-Al systems

In this chapter, the hardness of IMCs in the Fe-Zn binary and the Fe-Zn-Al ternary systems was evaluated from each phase in the multi-phase alloys obtained by the alloying method. In the Fe-Zn binary system, the hardnesses of Γ_1, δ_{1p} and ζ hardly depend on temperature and composition, but those of the Γ and δ_{1k} show an obvious composition dependence. On the other hand, although some of the hardness data are missing, that of each IMC formed in the Fe-Zn-Al ternary system is slightly lower than that of the same IMC in the Fe-Zn binary system. On the other hand, the brittleness of each IMC in the ternary system is much higher than that in the binary system.

Chapter 6 : Experimental study on the interfacial reaction between solid Fe and molten Zn

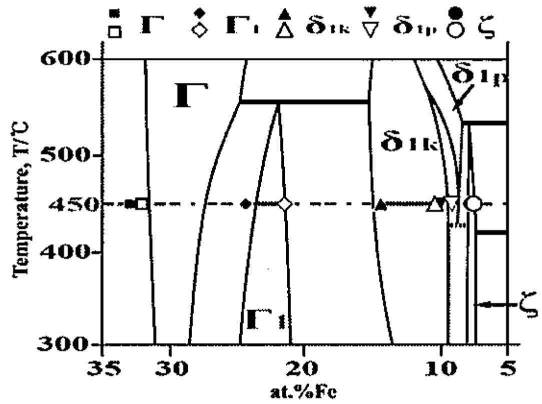

Figure 5 Interface compositions of IMC layers after hot-immersion for 5days. Measured values are plotted on the experimentally determined equilibrium phase diagram by alloying method

In this chapter, the formation behavior of IMC layers in the Fe / Zn interface was investigated by a simple dipping experiment, in which considering the preheating of steel plate before dipping and the suppression of convection in molten Zn at the time of dipping were considered. Especially, formation behavior of the IMCs in the initial stage was clarified and the deviation from the equilibrium concentration in the interface composition after various dipping time was also carefully examined by microstructural observation and FE-EPMA/WDS analysis. It was found that Γ was firstly formed and then δ_{1k}, ζ, δ_{1p} and Γ_1 were formed in order of precedence. Meanwhile, while interface concentrations of Γ_1, δ_{1k} ζ and liquid were gradually closed to their equilibrium compositions, those of Γ and δ_{1p} did not reach the equilibrium composition even by long time dipping as shown in figure 5. Especially, the interface composition of Γ is extremely deviated from the equilibrium one to Fe-rich direction after long reaction time for 5days.

Chapter 7 : Conclusion

In this chapter, the contents of chapter 1 through 6 are summarized.

Reference

[1] U.R Kattner, B.P Burton, Phase diagrams of binary iron alloys, H. Okamoto, ASM International, Materials Park, OH, 1993. P.12.

[2] B. P. Burton, P. Perrot, Phase Diagram of Binary Iron Alloys, ed. By H. Okamoto, ASM Int., Material Park, OH, (1993) 459

[3] P. Perrot, J. C. Tissier, J. Y. Dauphin, Z. Metallkde., 83 (1992) 11

論文審査結果の要旨

Zn-Al 浴に浸漬した後、短時間熱処理を加える合金化溶融亜鉛メッキは、自動車用鋼板の防食技術として広く利用されている。しかし、合金化中のメッキ膜における金属間化合物の形成は、秒単位で生じる非平衡プロセスであり、学術的理解が遅れている。特に、非平衡を論ずるためにも基礎情報として重要な Zn-Fe および Zn-Al-Fe 系平衡状態図は、過去の報告に不一致が多く、従来利用されてきた拡散対法ではなく、平衡に近い結果が期待できる多相合金法を利用した精密な実験が切望されている。そこで、本研究では、Al-Fe、Zn-Fe、Zn-Al-Fe 系状態図を FE-EPMA を用いた多相合金法により決定した。また、溶融純 Zn に純 Fe 板を浸漬した固液拡散対を作製し、各化合物相の核生成・成長挙動や異相界面組成の浸漬時間依存性を明らかにすると共に、合金法で決定した平衡組成との比較を行った。

第 1 章は序論である。

第 2 章では、Al-Fe 2 元系状態図における約 50 at%Al 以上の領域を実験的に決定した。高温域にしか存在しない ε 相を含め、従来の状態図において点線で表示されてきた ζ-$FeAl_2$、η-Fe_2Al_5、θ-Fe_4Al_{13} 金属間化合物相の単相領域を精密に決定した。その結果、ζ、η、θ 各金属間化合物相では、高温になるにつれて単相域が全体的に Fe 側にシフトすることを明らかにした。

第 3 章では、Zn-Fe 2 元系状態図における全領域を実験的に決定した。合計で 5 種類の安定な金属間化合物相が存在し、従来から不明瞭だった δ_{1p}-$FeZn_{10}$ 相が δ_{1k}-$FeZn_7$ 相とは独立した相であること、さらに $\delta_{1p} \rightarrow \delta_{1k} + \zeta$-$FeZn_{13}$ で示される共析反応が 450℃付近に存在することを示した。また、Γ-Fe_4Zn_9 や Γ_1-$Fe_{11}Zn_{40}$ 相の単相域は、従来の状態図より数%Fe 側にずれていることを明確にした。

第 4 章では、Zn-Al-Fe 3 元系状態図の 450℃等温断面を決定した。状態図の構成や平衡組成は、Perrot らによるものと近いが、3 元化合物 Γ_2-$Fe_8Zn_{87}Al_4$ 相の単相域はより狭いことを示した。

第 5 章では、Zn-Fe および Zn-Al-Fe 系状態図の決定のために作製した多相組織試料を利用して、各金属間化合物相のビッカース硬度を調査した。化合物相の硬度は、おおよそ $\Gamma_1 > \delta_{1k} > \Gamma > \delta_{1p} > \Gamma_2 > \zeta$ の順となった。また、硬さの組成依存性を調査したところ、Γ 相では Zn 濃度が増えるに従い硬度が上がるのに対し、δ_{1k} では下がることを示した。さらに、いずれの化合物においても、Al の添加により硬度は低下した。圧痕周辺の組織観察より、Γ と ζ には靱性があることを明らかにした。

第 6 章では、450℃の溶融純 Zn に予加熱した純 Fe 板を浸漬した固液拡散対により、各化合物相の核生成・成長挙動や異相界面組成の浸漬時間依存性を調査した。その結果、化合物相は 2 元系において、$\Gamma \rightarrow \delta_{1k} \rightarrow \zeta \rightarrow \delta_{1p} \rightarrow \Gamma_1$ の順に形成することを明確にした。また、各異相界面組成は浸漬時間に依存して変化し、特に Γ 相の存在組成域は、長時間の浸漬後でも第 3 章で決定した平衡状態から Fe 側に大きく偏倚していることを示した。

第 7 章は結論である.

以上、本論文は、Zn-Fe 基合金について、メッキ組織を制御するために最も基礎となる状態図の決定を行い、固液拡散対の結果と比較することでメッキ層における各化合物相の形成過程を明らかにした。本結果は、Zn-Al 浴を利用する自動車用鋼板に対して直接利用できないものの、その組織形成を考察する上で必要な基礎的かつ重要な多くの知見を含んでいる。以上のように、本論文は博士論文として充分な学術的独創性と工学的有用性を有しており、金属フロンティア工学発展への寄与が少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める.